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(54) Title: WATERFAST INK RECEPTIVE COATINGS FOR INK JET PRINTING, METHODS OF COATING SUBSTRATES UTILIZING SAID COATINGS, AND MATERIALS COATED WITH SAID COATINGS

(57) Abstract: Media coatings for use on substrates for ink jet printing include a cationically modified clay, a cationically modified silica and a binder. Alternatively, the media coatings also include additional additives. The ratio of cationically modified clay to cationically modified silica varies in the coating formulation from about 1 % to about 99 %. Desirably, the ratio of the cationically modified clay to cationically modified silica varies from about 10 % to about 50 %. More desirably, the ratio of cationically modified clay to cationically modified silica varies from about 25 % to about 35 %. The ratio of the total cationically modified clay and cationically modified silica to binder varies from about 20 % to about 80 %. Desirably, the ratio of the total cationically modified clay and cationically modified silica to binder varies from about 65 % to about 75 %.

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WATERFAST INK RECEPTIVE COATINGS FOR INK JET PRINTING, METHODS OF COATING SUBSTRATES UTILIZING SAID COATINGS, AND MATERIALS COATED WITH SAID COATINGS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is related to and claims priority from United States Provisional Patent Application Serial No. 60/177,074, filed January 19, 2000.

FIELD OF THE INVENTION

The present invention relates to coating formulations for paper, film and other substrates which are receptive to common, aqueous ink jet inks and form images exhibiting superior quality when compared to uncoated paper, film and other printable substrates. More specifically, the present invention relates to cationically modified coatings which render the printed images waterfast. The present invention also relates to methods of coating various printable substrates utilizing said coatings as well as materials coated with said coatings.

BACKGROUND OF THE INVENTION

The ink jet method of printing is a rapidly growing, commercially important printing process because of its ability to produce economical, high quality, multi-colored prints. In fact, ink jet print methodology is becoming the print method of choice for producing colored hard copy of computer generated images consisting of graphics and fonts in both narrow and wide format. Ink jet printing is a non-impact and non-contact printing method in which an electronic signal controls and directs droplets or a stream of ink that can be deposited on a wide variety of substrates. Current ink jet printing technology involves forcing the ink drops through small nozzles by piezoelectric pressure, thermal ejection, or oscillation, and onto the surface of a material/media. Ink jet printing is extremely versatile in terms of the variety of substrate material that can be treated, as well as the print quality and the speed

of operation that can be achieved. In addition, ink jet printing is digitally controllable.

For these reasons, ink jet printing methodology has been widely adopted for industrial marking and labeling. In addition, ink jet printing methodology has also found widespread use in architectural and engineering design applications, medical imaging, office printing (of both text and graphics), geographical imaging systems (e.g., for seismic data analysis and mapping), signage, in display graphics (e.g., photographic reproduction, business and courtroom graphics, graphic arts), and the like. Finally, ink jet printing has now also been used to create an image on a variety of textile substrates.

Both dyes and pigments have been used as colorants for such ink jet ink formulations. However, such materials do not always adhere well to the substrates to which the ink is applied. For example, dyes may dissolve upon a printed substrate's contact with water. Thus, images applied employing ink jet printing methodology may tend to run or smear upon repeated contact, or may be actually removed from the printed surface if exposed to substantial quantities of aqueous media (e.g., if an ink jet printed article is exposed to water or comes in contact with water through other means). There is therefore a need in the art for coatings which enhance the waterfastness capabilities of various substrates, in particular when aqueous based inks are to be employed on said substrates. It is to such need that the present invention is directed as the coatings of the present invention have proven particularly effective in improving waterfastness.

SUMMARY OF THE INVENTION

In accordance with the present invention, media coatings for use on substrates for ink jet printing include a cationically modified clay, a cationically modified silica and a binder. Alternatively, the media coatings also include additional additives. In particular, in one embodiment of the invention, the media coatings also include a surfactant. The ratio of cationically modified clay to cationically

modified silica varies in the coating formulation from about 1 % to about 99%. Desirably, the ratio of the cationically modified clay to cationically modified silica varies from about 10 % to about 50 %. More desirably, the ratio of cationically modified clay to cationically modified silica varies from about 25 % to about 35 %. The ratio of the total cationically modified clay and cationically modified silica to binder varies from about 20 % to about 80 %. Desirably, the ratio of the total cationically modified clay and cationically modified silica to binder varies from about 65% to about 75%.

These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there are waterfast ink receptive coatings for ink jet printing including a cationically modified clay and a cationically modified silica. These formulations use a blend of cationic clay and cationic silica in combination with binder(s), and optionally surfactants and other additives, to deliver superior image quality and waterfastness.

The coating formulations may be used with paper, film, scrim and other printable substrates which are receptive to common, aqueous ink jet inks and form images exhibiting superior quality to uncoated paper, film or other substrates or to substrates which have merely been coated with either cationically modified clay, or cationically modified silica. Preferred substrates for use with the coating include films known as synthetic papers such as those available from the Oji Yuka Synthetic Paper Corporation and marketed by Kimberly-Clark under the designation Kimdura®. Such substrates are preferred for purposes of waterfastness, since they do not appear to swell or cockle. In particular, Kimdura® synthetic paper having a thickness of 150 microns may be easily used. Other Kimdura® materials such as those

having thicknesses of between approximately 60 and approximately 500 microns also may be readily used. It is important that such substrates be able to easily feed through an ink jet printer.

Other films which may be coated with the coating of the present invention include polyester and vinyl films. Other substrates which may be coated with the coating of the present invention include latex saturated paper substrates. Further, such coatings may also be applied to nonwoven substrates, such as those made from polyolefins as well as woven substrates.

Printed images on the ink jet media coating are rendered waterfast, resisting deterioration of the image upon repeated exposure to water. This quality may be developed within hours or minutes from the completion of printing. Exposure to water may be accomplished by placing the printed sample under dripping or running water, or even submersion in water for a limited period of time.

As previously stated, the coating formulation in the present invention utilizes a combination of both a cationically modified clay and a cationically modified silica. An example of such a cationically modified clay may be obtained from ECC International of Atlanta, Georgia under the designation Astra-Jet™. The cationically modified clay consists of an aqueous dispersion of Kaolin and a polyquartenary amine. While, ECCI markets a line of Astra-Jet™ clays, the original clay composition is desirable for the purpose of the coating of the present invention.

The cationically modified silica may consist of an aqueous silica dispersion including a cationic polymer similar to that described above. Alternatively, the cationic silica may consist of an aqueous amorphous silica stabilized with alumina and other additives, such as the cationic silica gel dispersion sold by Grace Davison of Columbia, Maryland under the designation Cationic Sylojet P612, with a cationic surface

modifier. An unmodified silica is available from Grace Davison under the designation Sylojet P612.

The ratio of cationically modified clay to cationically modified silica may vary in the coating formulation from about 1 % up to about 99 % by weight. Desirably, the ratio of the cationically modified clay to cationically modified silica may vary from about 10 % to about 50 % by weight. More desirably, the ratio of cationically modified clay to cationically modified silica may vary from about 25 % up to 35 % by weight.

The formulation further includes a binder. Such a binder serves to both bind the clay and silica together (pigment particles), and also to bind the coating to a media substrate. The binder may be comprised of any film forming, water insoluble polymer, providing the polymer is compatible with the cationic clay and silica. Binders which are suitable for the formulation include, but are not limited to nonionic latexes composed of polymers of vinyl acetate, ethylene vinyl acetate, acrylates, and acrylate-vinyl acetate. Other polymer materials which are suitable as binders include styrenics such as styrene rubbers (SBR), styrene maleic anhydride (SMA); and styrene acrylonitrile (SAN). Cationic latexes may also be employed as a suitable binder. ? Further, mildly anionic latexes may also be used as a binder. Strongly anionic latexes would be unacceptable binders however, as they would coagulate with the other cationic materials. The ratio of the total pigment, that is the combination of cationically modified clay and cationically modified silica, to the coating binder may vary from about 20 % up to about 80 %. Desirably, the ratio of the total pigment to the coating binder may vary from about 65 % to about 75 %.

In addition to the clay, silica and binder, optional additives may be added to improve the performance of the coatings. For instance, UV absorbers/light stabilizers may be added to improve light fastness. Additionally, surfactants or wetting agents may be added as well. Desirably, if such surfactants are utilized they are nonionic, cationic or

zwitterionic. Examples include Triton X100 and Tergitol both from Union Carbide. Further, a leveling agent such as an aliphatic diol may be used as well. Other optional additives include flow modifiers, and optical whiteners and/or brighteners.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or the scope of the present invention. Unless stated otherwise, all percents are percents by weight. An example of a coating formulation of the present invention, for use on a variety of media substrates is expressed in Table 1. An example of a control coating formulation, without a cationically modified silica, is described in Table 2. The particle size of the following Sylojet P612 silica materials is approximately 12 microns. The clay and silica are present in aqueous dispersions.

Table 1

Example of Cationically Modified Clay and Cationically Modified Silica Coating of the Present Invention

(Sample identified as Coating "A" for testing)

Ingred.	%solids	Parts Dry	Parts Wet	Wt%dry	Wt%wet	Wet Batch x1.5
Water		0.0	0.0	0.0	0.0	0.0
Cationic Sylojet P612 Silica[a]	29.4	53.0	180.3	52.4	18.2	270.4
Astrajet Clay	35.2	22.5	63.9	22.3	7.7	95.9
Q2 5211	100.0	0.6	0.6	0.6	0.21	0.9
Airflex 540	54.8	25.0	45.6	24.7	8.6	68.4
Total		101.1	290.4			435.6

Notes:

a. Cationic Sylojet P612 Silica is cationically modified silica.

For the purposes of the coating described above, the Q2 5211 is an ethoxylated polysiloxane surfactant and was obtained from Dow Corning. The Airflex 540 is an ethylene vinyl acetate (EVA) latex binder available from Air Products. The pigment to binder ratio (P/B) for the sample was 0.75:1, and the percent total solids (%TS) was 34.8%, by weight.

Table 2

Example of Cationically Modified Clay and Unmodified Silica Coating of the Present Invention

(Sample identified as Coating "C" for testing)

Ingred.	%solids	Parts Dry	Parts Wet	Wt%dry	Wt%wet	Wet Batch x1.5
Water		0.0	0.0	0.0	0.0	0.0
Sylojet P612 Silica[a]	26.7	53.0	198.5	52.4	17.2	297.8
Astrajet Clay	35.2	22.5	63.9	22.3	7.3	95.9
Q2 5211	100.0	0.6	0.6	0.6	0.19	0.9
Airflex 540	54.8	25.0	45.6	24.7	8.1	68.4
Total		101.1	308.6			463.0

Notes:

a. Sylojet P612 Silica is non-cationically modified silica.

The pigment to binder ratio (P/B) for the sample was 0.75:1, and the percent total solids (%TS) was 32.8%, by weight.

Drawdown

Generally, for each of the coatings of the examples, the components were combined in the order shown using a plastic beaker

and a paddle-type mixer. Draw downs using the Meyer Rod method (as is known to those of ordinary skill in the art) were made with a # 28-30 meyer rod on Kimdura® FPG 150 (for 150 micron) available from Kimberly-Clark, to yield a coat weight of between approximately 5.5 to 6.0 lbs/1300 sq. ft. (20 gsm to 23 gsm). The coated sample sheets of 10 by 12 inch size were then cut to 8.5 by 11 inch size to facilitate printing and testing.

The specific drawdown procedure employed is described as follows. A 10 x 12 inch sheet of paper or film (e.g. Kimdura® FPG 150) was placed on a flat surface. A wire-wound (Meyer) rod was placed on top of the sheet and 2kg weights were placed on the ends of the rod to prevent slipping. The coating was poured on the substrate such that it contacted the rod and formed a narrow pool the width of the substrate. The substrate was drawn under the rod and the coating was spread evenly along the length of the sheet. It should be recognized that different coat weights may be obtained by utilizing rods wound with different size wires.

Alternatively coatings may be applied to substrates via other coating methods known to one of ordinary skill in the art, such as the Air Knife method or the Slot Dye method. Other coating methods include the gravure roll, and reverse roll coating methods. Coatings may be applied at levels from about 5 to about 45 grams per square meter (gsm). Desirably, the coatings are applied at between about 15 to about 35 gsm. The samples were then placed in a conventional forced air oven at approximately 75° C for about 3-5 minutes to allow to dry. The samples were stored in ambient room conditions (20-25° C) overnight prior to printing.

The dried samples were then printed with the indicated printers and settings as shown in Tables 3-5 which follow.

Printing

Color blocks of the colors Cyan (C), Magenta (M), Yellow (Y), Black (K), Red (R), Green (G), and Blue (B) were printed from Microsoft ® MS Paint block pattern in a 2 x 5 inch pattern on the Kimdura® sheets. The color blocks were printed with inks provided with each printer. A white (unprinted) block was also included in the 2 x 5 inch pattern. The printers used included a Hewlett-Packard 722C on HP Premium Ink Jet Paper/Best Settings, an Epson 850 on Photo Quality Ink Jet Paper/720dpi/Automatic Settings and a Canon 4200 printer on Hi Resolution Paper/Standard/No Color Matching Settings. Following printing, samples were dried overnight under ambient conditions before further testing. Following printing and drying, the samples were cut out into their respective 2 x 5 inch block patterns.

Soak Testing

The cut out 2 x 5 inch samples were placed in a 2 liter plastic beaker containing 2 liters deionized water at 20°C for 24 hours. Samples were clamped to the side of the container such that the entire test pattern remained submerged for the duration of the test. After this period had elapsed, samples were removed and placed flat on a KimWipes® wiper. KimWipes are wipers available from the Kimberly-Clark Corporation. The surfaces of the samples were gently dried with a KimWipe® wiper. The samples were allowed to dry completely before spectral measurements were taken (minimally 2-3 hours). An X-Rite® Model 938 Spectrodensitometer was used to perform L*a*b* spectral measurements, the CIE LAB measurement being one known to one of ordinary skill in the art. The X-Rite spectrodensitometer was obtained from the X-Rite corporation of Grandville, Michigan. In performing the measurements, the illuminant type was a D_{50} and the observer being 2°.

The degree of optical lightening resulting from exposure to water was measured quantitatively using L*a*b* values. Delta E* is calculated in accordance with the following equation:

$\Delta E^* = \text{SQRT}\ [(L^*\text{standard} - L^*\ \text{sample})^2 + (a^*\text{standard} - a^*\ \text{sample})^2 + (b^*\text{standard} - b^*\ \text{sample})^2]$,

where the standard is representative of the value for the sample that has not been soaked.

The higher the Delta E* (hereinafter ΔE*), the greater the change in color intensity. A large increase in delta E* would typically be indicative of fading, washout or bleed of dye. In running the L*a*b* test on the samples, controls of each coating were used as a basis for comparison. The control samples (STD) were just printed with the respective formulations, as opposed to being printed and soaked. More extensive bleeding of the dyes was observed when the unmodified silica was utilized in the tested samples, *i.e.* Formulation "C".

Table 3

Print Results for Hewlett Packard 722 Printer

Sample #	Coating	Printer	Print Mode	Color	ΔE* 24 hr soak	Avg. ΔE*
1	A	HP 722	HP Prem.IJ Paper /Best	K	0.19	
				W	2.81	
				B	4.37	
				C	8.36	
				G	16.11	
				Y	14.31	
				R	2.9	
				M	0.74	6.22
2	C	HP 722	HP Prem. IJ Paper /Best	K	0.23	
				W	7.40	
				B	22.82	
				C	11.72	
				G	12.78	
				Y	24.71	
				R	6.49	
				M	6.58	11.59

Table 4

Print Results for Canon 4200 Printer

Sample #	Coating	Printer	Print Mode	Color	ΔE* 24 hr soak	Avg. ΔE*
3	A	Canon 4200	Hi. Res. Paper/ Standard	K	2.94	
				W	0.43	
				B	2.41	
				C	1.33	
				G	5.37	
				Y	3.25	
				R	2.36	
				M	3.09	2.65
4	C	Canon 4200	Hi. Res. Paper/ Standard	K	1.18	
				W	0.39	
				B	3.82	
				C	2.63	
				G	3.39	
				Y	5.58	
				R	2.27	
				M	7.3	3.32

Table 5

Print Results for Epson 850 Printer

Sample #	Coating	Printer	Print Mode	Color	ΔE* 24 hr soak	Avg. ΔE*
5	A	Epson 850	Photo Qual IJ Paper/ 720 dpi	K	2.41	
				W	0.66	
				B	5.44	
				C	4.79	
				G	3.48	
				Y	3.92	
				R	1.25	
				M	1.81	2.97
6	C	Epson 850	Photo Qual IJ Paper/ 720 dpi	K	3.17	
				W	0.84	
				B	18.42	
				C	4.03	
				G	11.15	
				Y	4.18	
				R	18.58	
				M	7.87	8.53

From the data it can be seen that use of a coating including both a cationically charged clay and cationically charged silica (Coating A) enhances waterfastness of an ink jet printed image on a coated substrate, as measured by a spectrodensitometer. For instance, in observing data from the Epson 850 printer, the red ΔE* values for the control (Coating C) compared with the cationic clay/silica combination (Coating A) demonstrates a significant difference in light fastness.

While the invention has been described in detail with particular reference to a preferred embodiment thereof, it should be understood that many modifications, additions, and deletions can be made thereto without departure from the spirit and the scope of the invention as set forth in the following claims.

What is claimed is:

1. A media coating which demonstrates waterfastness following ink jet printing, said media coating comprising:

a cationically modified silica;

a cationically modified clay; and

a binder.

2. The media coating according to claim 1, wherein the cationically modified clay comprises an aqueous dispersion of Kaolin and a polyquaternary amine.

3. The media coating according to claim 1, wherein the cationically modified silica comprises an aqueous silica dispersion including a polyquaternary amine.

4. The media coating according to claim 1, wherein the cationically modified silica comprises aqueous amorphous silica stabilized with alumina.

5. The media coating according to claim 4, comprising in addition, a cationic surface modifier.

6. The media coating according to claim 1, wherein the binder comprises a film forming, water insoluble polymer that is compatible with the cationic clay and the cationic silica.

7. The media coating according to claim 6, wherein the binder is selected from the group consisting of nonionic latexes comprising polymers of vinyl acetate, ethylene vinyl acetate, acrylates, acrylate vinyl acetate; styrenics comprising styrene rubbers (SBR), styrene maleic anhydride (SMA), and styrene acrylonitrile (SAN); cationic latexes; mildly anionic latexes; and mixtures thereof.

8. The media coating according to claim 7, wherein the weight ratio of clay to silica is from about 1% to about 99%.

9. The media coating according to claim 8, wherein the weight ratio of clay to silica is from about 10% to about 50%.

10. The media coating according to claim 9, wherein the weight ratio of clay to silica is from about 25% to about 35%.

11. The media coating according to claim 1, wherein the weight ratio of total clay and silica to binder is from about 20% to about 80%.

12. The media coating according to claim 11, wherein the weight ratio of total clay and silica to binder is from about 65% to about 75%.

13. The media coating according to claim 1, comprising in addition, one or more materials selected from the group consisting of UV absorbers/light stabilizers, surfactants, wetting agents, leveling agents, flow modifiers, optical whiteners, and brighteners.

14. The media coating according to claim 13, comprising a surfactant that is selected from the group consisting of nonionic, cationic, and zwitterionic surfactants.

15. The media coating according to claim 13, wherein the media coating comprises a leveling agent, wherein the leveling agent comprises aliphatic diol.

16. A media coating which demonstrates waterfastness following ink jet printing, said media coating comprising a cationically modified silica; a cationically modified clay; and a binder, where said media coating has an average ΔE^* for cyan, magenta, yellow, black, red, green, and blue ink jet printing inks after soaking in de-ionized water at 20°C for 24 hours that is no more than 80% of the average ΔE^* for a control media coating which is free of cationically modified silica.

17. A method of coating a substrate comprising applying to a substrate a coating comprising a cationically modified silica; a cationically modified clay; and a binder.

18. The method of coating a substrate according to claim 17, wherein the substrate is selected from the group consisting of paper, film and scrim.

19. The method of coating a substrate according to claim 18, wherein the paper comprises synthetic paper that can feed through an ink jet printer.

20. The method of coating a substrate according to claim 19, wherein the synthetic paper has a thickness of from about 60 to about 500 microns.

21. The method of coating a substrate according to claim 20, wherein the synthetic paper has a thickness of about 150 microns.

22. The method of coating a substrate according to claim 18, wherein the substrate comprises a material selected from the group consisting of nonwoven substrate, woven substrate, polyester film, vinyl film, and latex saturated paper.

23. The method of coating a substrate according to claim 22, wherein the substrate comprises a nonwoven substrate comprising a polyolefin.

24. A coated substrate comprising a substrate and a coating comprising a cationically modified silica; a cationically modified clay; and a binder.

25. The coated substrate according to claim 24, wherein the cationically modified clay comprises an aqueous dispersion of Kaolin and a polyquaternary amine.

26. The coated substrate according to claim 24, wherein the cationically modified silica comprises an aqueous silica dispersion including a polyquaternary amine.

27. The coated substrate according to claim 24, wherein the cationically modified silica comprises aqueous amorphous silica stabilized with alumina.

28. The coated substrate according to claim 24, wherein the binder comprises a film forming, water insoluble polymer that is compatible with the cationic clay and the cationic silica.

29. The coated substrate according to claim 28, wherein the binder is selected from the group consisting of nonionic latexes

comprising polymers of vinyl acetate, ethylene vinyl acetate, acrylates, acrylate vinyl acetate; styrenics comprising styrene rubbers (SBR), styrene maleic anhydride (SMA), and styrene acrylonitrile (SAN); cationic latexes; mildly anionic latexes; and mixtures thereof.

30. The coated substrate according to claim 24, wherein the weight ratio of clay to silica is from about 1% to about 99%.

31. The coated substrate according to claim 30, wherein the weight ratio of clay to silica is from about 10% to about 50%.

32. The coated substrate according to claim 31, wherein the weight ratio of clay to silica is from about 25% to about 35%.

33. The coated substrate according to claim 24, wherein the weight ratio of total clay and silica to binder is from about 20% to about 80%.

34. The coated substrate according to claim 33, wherein the weight ratio of total clay and silica to binder is from about 65% to about 75%.

35. The coated substrate according to claim 24, comprising in addition, one or more materials selected from the group consisting of UV absorbers/light stabilizers, surfactants, wetting agents, leveling agent, flow modifiers, optical whiteners, and brighteners.

36. The coated substrate according to claim 35, comprising a surfactant that is selected from the group consisting of nonionic, cationic, and zwitterionic surfactants.

37. The coated substrate according to claim 35, wherein the media coating comprises a leveling agent, wherein the leveling agent comprises aliphatic diol.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: WATERFAST INK RECEPTIVE COATINGS FOR INK JET PRINTING MATERIALS AND COATING METHODS THEREWITH

(57) Abstract: Media coatings for use on substrates for ink jet printing include a cationically modified clay, a cationically modified silica and a binder. Alternatively, the media coatings also include additional additives. The ratio of cationically modified clay to cationically modified silica varies in the coating formulation from about 1 % to about 99 %. Desirably, the ratio of the cationically modified clay to cationically modified silica varies from about 10 % to about 50 %. More desirably, the ratio of cationically modified clay to cationically modified silica varies from about 25 % to about 35 %. The ratio of the total cationically modified clay and cationically modified silica to binder varies from about 20 % to about 80 %. Desirably, the ratio of the total cationically modified clay and cationically modified silica to binder varies from about 65 % to about 75 %.

WO 01/53107 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/02003

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B41M5/00 C09D123/08 C09D131/04 D06P5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B41M C09D D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198703 Derwent Publications Ltd., London, GB; Class A97, AN 1987-018948 XP002169433 & JP 61 277481 A (CANON KK), 8 December 1986 (1986-12-08) abstract ———	1,16,17, 24
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 056 (M-0929), 31 January 1990 (1990-01-31) & JP 01 281982 A (CANON INC), 13 November 1989 (1989-11-13) abstract ———	1,16,17, 24

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 2001	11/07/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Markham, R

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/02003

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 709 223 A (CANON KK) 1 May 1996 (1996-05-01) page 3, line 8 - line 14 page 4, line 52 -page 5, line 15	1,16,17, 24

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

International Application No. PCT/US 01 02003

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 16 (part)

Present claim 16 relates to a product defined by reference to the parameter Delta E* as defined in the present description (page 10, lines 2-7).

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare this parameter, which the applicant has chosen to employ, with what is set out in the prior art. This lack of clarity is such as to render a meaningful complete search over the area encompassed by present claim 16 impossible. Consequently, the present search has been restricted by limiting the search of claim 16 to the coating "A" described in the example (see Table 1) in the present description.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 01/02003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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